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The funds provided by this grant (DAAH04-93-G-0459) were used to purchase four IBM workstations and related equipment. This equipment augmented a system of workstations that serves a research group of graduate students and postdoctoral fellows. The focus of the research is on developing methods and carrying out chemical dynamics simulations of fundamental processes to obtain a better understanding of the chemical behavior of energetic materials.

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**THEORETICAL CHEMICAL DYNAMICS STUDIES OF REACTIONS IN
ENERGETIC MATERIALS**

FINAL REPORT

(Report Period: September 1, 1993 - August 31, 1995)

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Table of Contents

SUMMARY	3
RESEARCH	4
PUBLICATIONS, REPORTS, AND THESES	6
PERSONNEL	8

SUMMARY

The funds provided by this grant (DAAH04-93-G-0459) were used to purchase four IBM workstations and related equipment. This equipment augmented a system of workstations that serves a research group of graduate students and postdoctoral fellows. The focus of the research is on developing methods and carrying out chemical dynamics simulations of fundamental processes to obtain a better understanding of the chemical behavior of energetic materials.

RESEARCH

This research program is concerned with the development of computational methods (mainly, classical and semiclassical) and calculations for simulating chemical reactions in many-atom systems. The particular processes of interest are those that occur in the initial stages of the decomposition of energetic materials that are based on nitramines. The long-range goal is the development of theoretical/computational methods for investigating reactions in condensed-phase energetic materials.

The new equipment provided by this grant has allowed for more extensive studies of the systems of interest. The unimolecular decomposition of RDX is central to the overall project, and thus we have continued our studies of this process. We have developed a more accurate potential-energy surface for the decomposition of isolated RDX molecules, studied the fundamental nature of the intramolecular dynamics of RDX, and studied the unimolecular decomposition of methylene nitramine (a primary decomposition product of RDX in the gas phase). In addition to these studies, we have studied the effects of crossings of transition states on mode mixing (IVR), carried out some calculations to develop practical methods for computing tunneling effects in polyatomic systems, and have done some preliminary dynamics calculations for the decomposition of HMX. In a collaboration with Drs. Cary Chabalowski and Betsy Rice at ARL, we have done some preliminary *ab initio* calculations of the effects of the dielectric constants of solvents on RDX.

In an earlier study [Sewell and Thompson, J. Chem. Phys. **95**, 6228 (1991)] we developed a potential-energy surface (PES) for the decomposition of isolated RDX molecules and carried out classical trajectory calculations for comparisons with irmpd/molecular beam results. We have made improvements in the PES and carried out more extensive dynamics calculations. A paper on this study has been accepted for publication in the Journal of Physical Chemistry.

Methylene nitramine (CH_2NNO_2) is a primary product of RDX decomposition in the gas phase. A thorough interpretation of the results of the Zhao *et al.* irmpd experiments requires an understanding the decomposition of this fragment formed in the

RDX ring fission reaction. In collaboration with Betsy Rice, George Adams, and others at ARL, we have developed a global, analytical PES based on *ab initio* results. We have used this PES to carry out two dynamics studies. The first study focused on calculating the branching of the two decomposition reactions for microcanonical conditions [J. Phys. Chem. **99**, 5016 (1995)] while the second was concerned with mode selective behavior [J. Chem. Phys. **102**, 8790 (1995)]. Two papers have been published and three ARL reports have also been written [Technical Reports ARL-TR-680, ARL-TR-691, and ARL-TR-740].

Many of the reactions in energetic materials involve H-atom migration (such as the elimination of HONO in nitramines and nitro alkanes). This process usually involves a simple barrier on the order of 40-60 kcal/mol. Thus, at low temperatures tunneling may be a factor in the stability of these compounds. We have been investigating methods for treating tunneling in multidimensional systems. This is a problem of general interest in chemistry. We have been using semiclassical methods because a purely quantum mechanical method would be feasible for large systems. We have reported the results of calculations of tunneling splitting in planar and full three-dimensional models of malonaldehyde [Chem. Phys. Letters **224**, 470 (1994); J. Chem. Phys., in press]. The results are in excellent agreement with experiment. This demonstrates the power of this approach. We have follow this with a study of tunneling in HONO *cis-trans* isomerization [J. Chem. Phys. **100**, 6445 (1994)]. In all of these studies, we investigated the effects of heavy atom motions and vibrational mode selectivity on tunneling.

We have continued our studies of IVR since an understanding of the reaction dynamics of polyatomic systems require an understanding of how energy flows among the various vibrational modes and into the reaction coordinate mode. We completed two studies of IVR in this report period, which have been published. In one of these, we reported a method for computing classical intramolecular mode-to-mode energy transfer rates that uses Fourier transforms of trajectory results [J. Phys. Chem. **98**, 6817 (1994)]. We have also done extensive calculations to investigate the effects of passages over transition states on IVR in molecules [Chem. Phys. Letters **218**, 166 (1994)]. Specifically, we examined line broadening and shifting due to repeated crossings of a transition state.

If this effect could be “isolated” in spectroscopic measurement in the laboratory it would provide a method of extracting reaction rates from ir spectra.

Hartree-Fock self-consistent-field methods coupled with Onsager theory were used to study the changes in the molecular properties of RDX induced by solvents of varying dielectric constants. Changes in geometric parameters, harmonic vibrational frequencies, Gibbs free energy, infrared and Raman spectral intensities, atomic charge distributions, and dipole moments were calculated. [P. J. Zahner, M.S. Thesis, OSU, 1995]

PUBLICATIONS, REPORTS, AND THESES

PUBLICATIONS

- Candee C. Chambers and Donald L. Thompson,
“Enhancement of Vibrational Mode Mixing Due to Isomerization Barrier Crossings,”
Chem. Phys. Letters **218**, 166-174 (1994).
- Yue Qin and Donald L. Thompson,
“Tunneling Effects in HONO *Cis-Trans* Isomerization,”
J. Chem. Phys. **100**, 6445-6457 (1994).
- Xiao Yan Chang, Karen L. Bintz, Donald L. Thompson, and Lionel M. Raff,
“Classical Intramolecular Energy Transfer Rates Using Fourier Transform Methods: Four-Atom Systems,”
J. Phys. Chem. **98**, 6317-6323 (1994).
- Yin Guo, Thomas D. Sewell, and Donald L. Thompson,
“A Full-Dimensional Semiclassical Calculation of Vibrational Mode Selectivity in the Tunneling Splitting in a Planar Model of Molonaldehyde,”
Chem. Phys. Letters **224**, 470-475 (1994).
- Betsy M. Rice, George F. Adams, Michael Page, and Donald L. Thompson,
“Classical Dynamics Simulations of Unimolecular Decomposition of CH₂NNO₂: HONO Elimination vs. N-N Bond Scission,”
J. Chem. Phys. **99**, 5016-5028 (1995).
- Betsy M. Rice, John Grosh, and Donald L. Thompson,
“Vibrational Mode Selectivity in the Unimolecular Decomposition of CH₂NNO₂,”
J. Chem. Phys. **102**, 8790-8799 (1995).

- Candee C. Chambers and Donald L. Thompson,
"Further Studies of the Classical Dynamics of the Unimolecular Dissociation
of RDX,"
J. Phys. Chem., in press.
- Thomas D. Sewell, Yin Guo, and Donald L. Thompson,
"Semiclassical Calculations of Tunneling Splitting in Malonaldehyde,"
J. Chem. Phys., in press.
- Yin Guo, Thomas D. Sewell, and Donald L. Thompson,
"Analysis of the Zero-Point Energy Problem in Classical Trajectories,"
J. Chem. Phys., in press.
- Y. Guo, Y. Qin, D. C. Sorescu, and D. L. Thompson, "Multidimensional
Semiclassical Tunneling between Asymmetric Wells via Two Channels," J. Chem.
Phys., submitted.
- D. V. Shalashilin and D. L. Thompson, "Intrinsic Non-RRK Behavior: Classical
Trajectory, Statistical Theory, and Diffusional Theory Study of the Unimolecular
Dissociation of Dimethylnitramine," J. Chem. Phys., to be submitted.

REPORTS

- Betsy M. Rice, George F. Adams, Michael Page, and Donald L. Thompson,
"Analytical Potential Energy Surface for Methylene Nitramine (CH_2NNO_2),"
Techical Report ARL-TR-680, February 1995.
- Betsy M. Rice and Donald L. Thompson,
"Classical Dynamics Simulations of Unimolecular Decomposition of
 CH_2NNO_2 : HONO Elimination vs. N-N Bond Scission,"
Techical Report ARL-TR-691, February 1995.
- Betsy M. Rice, John Grosh, and Donald L. Thompson,
"Vibrational Mode Selectivity in the Unimolecular Decomposition of
 CH_2NNO_2 ,"
Techical Report ARL-TR-740, May 1995.

THESES

Candee Cae Chambers, Ph.D. Thesis (Oklahoma State University, July, 1994). *Dynamics of Polyatomic Molecules. I. Enhancement of Vibrational Mode Mixing due to Intramolecular Conversions. II. Chemical Reactions in Cyclic Nitramines.*

Paul Joseph Zahner, M.S. Thesis (Oklahoma State University, July, 1995). *Solvation of RDX as a Function of the Dielectric Constant of the Solvent.*

PERSONNEL

The equipment purchased by this grant is being used as part of a network of workstations that serves the PI's research group. Most of the personnel using the equipment are supported by ARO (Grant No. DAAH04-93-93-G-0450; and EPSCoR Grant No. DAAL03-92-G-0358). Part of the group is supported by AFOSR.

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